Rapid Bio-Oxidation Method of Waste Disposal

NANDOR PORGES
*Eastern Regional Research Laboratory**
Philadelphia 18, Pennsylvania

Breweries, as well as many other industrial installations, are becoming cognizant of the waste disposal problem. This is especially true if the brewery is not situated in a large city but is located on a stream that can no longer take the wastes, or is situated in a small community that is out-growing its waste treatment facilities. Under such conditions it will become necessary for a brewery to treat its own waste. A rapid bio-oxidation method developed for the disposal of dairy wastes may find application for the disposal of brewery wastes. Development and principles of this rapid biological oxidation have been described[9,16,17].

Waste waters from a brewery are not toxic. Problems are created because the stabilization of the organic matter present in the waste requires oxygen. The waste produced in the manufacture of one barrel of beer has been variously reported as having a population equivalent of 8.1[20], 12.4[3] and 19[1]. Thus the average amount of waste approximates the total pollution load of 13 people. The volume of waste is about 300 gallons per barrel of beer[1]. The extent and seriousness of the problem may be estimated for each brewery.

The sources of the sewered waste based on oxygen demand are waste wort 89%, starting vat 7.2%, carbon dioxide vat 3.6% and finishing tanks 0.2%[4]. Another analysis gave 76.2% of the pollution load caused by wash water, waste beer, cooling water and sanitary wastes, 3.5% by expellor liquor, 1.1% by hop press liquor, 4.6% by mash filter-cloth wash water, 1.3% yeast wash water, and 13.3% by beer filtrate from yeast[19].

Our studies on rapid oxidation were conducted on a synthetic dairy waste[18]. The composition of this waste and that from a brewery[3] are shown in Table I for comparative purposes. The composition of the waste will vary with each brewery depending on housekeeping practices, hidden losses and other factors. Similar results may be anticipated with this brewery waste as were obtained with dairy wastes. The B.O.D. to nitrogen ratio of the waste from this brewery was well within the 19 to 1 found necessary for optimum aerobic activity according to studies made on the nutritional requirements in the biological stabilization of industrial wastes[4]. However, supplementation of nitrogen and phosphorus may be required where insufficiencies exist.

TABLE I
Composition of Waste

	Brewery ppm	Dairy ppm
C.O.D.	1330*	1050
B.O.D.	890	703
Organic solids	1110	883
Sugars	280	505
Protein	460	369
Nitrogen	73	59
Carbon	498*	393*
B.O.D./N	12.2	11.9
C/N	6.8	6.3

*Calculated from B.O.D.

* A laboratory of the Eastern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture.

Fermenter Studies

Aerobic treatment of wastes is a means for converting a very dilute solution of fermentables of high oxygen demand to substances of little or no oxygen demand. It is the application of a natural process. The desirable changes occur so rapidly that quick chemical methods of analysis become necessary in order to follow these changes[18].

Aeration was easy to maintain in the fermenter used in these laboratory studies[11]. Synthetic waste fed continuously through the 5-gallon fermenter at the rate of 2-volume changes per day showed 40 to 50% reduction in C.O.D.[18]. However, most of the studies reported were made on a fill-and-draw procedure. When 1/5 of the mixed aerated solution served as seed for fresh waste, the results shown in Figure 1 were obtained[7]. About 50% of the original oxygen-demanding substances had disappeared. Separation of the solids or sludge gave over 90% reduction in C.O.D. These changes occurred within 6 to 8 hours. Analysis of the aerator influent and effluent of a continuous process gave a solids balance sheet[8]. Table II shows that only a small amount of carbohydrate remained in the sludge; in fact, all sugars were gone. The protein was also incorporated into sludge, producing clear supernatant solution. Actually ½ of the original organic matter was completely oxidized; the resulting sludge or microbial cells approximated 67% protein, 11% carbohydrate and 8% ash.

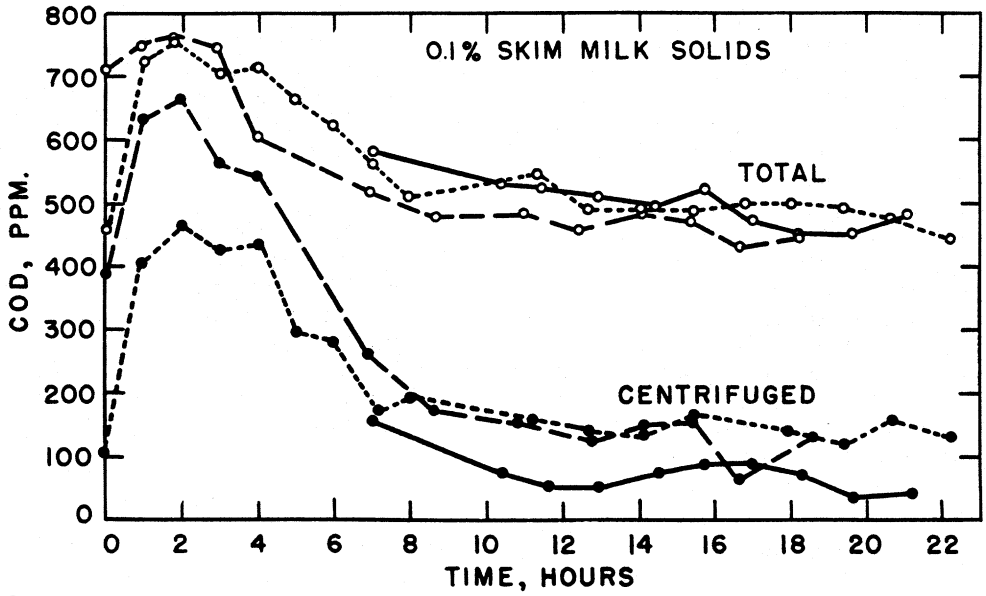

FIGURE 1. C.O.D. CHANGES IN FILL-AND-DRAW OPERATION (ABOUT 40% OF ADDED SKIM MILK C.O.D. OXDIZED IN 7 HOURS. STARTING SEED CONTAINED 500 PPM SLUDGE IN 1/5 OF FINAL VOLUME).

(Reprinted from the Proceeding of the 6th Industrial Waste Conference)

TABLE II
Solids Balance in Bio-Oxidation of Milk Waste
(based on dry skim milk)

	Protein %	Carbohydrates %	Total %
Influent	35	53	88
Effluent solids	34	7	41
Effluent solubles	1	2	3
Material destroyed	0	44	44

Manometric Studies

Details of these oxidation changes were obtained by means of the Warburg apparatus[5]. This was possible as it had been established that CO_2 was the only gas evolved in the biological oxidation of sewage[21]. The rate and extent of oxidation were followed at 30° C using 3 ml of well-aerated sludge containing 500 ppm solids. Figure 2 presents results obtained when 3 mg skim milk, 1.5 mg lactose and 1.05 mg protein were added. At first the oxygen demand was rapid, then decreased by the sixth hour to that of the sludge mixture alone.

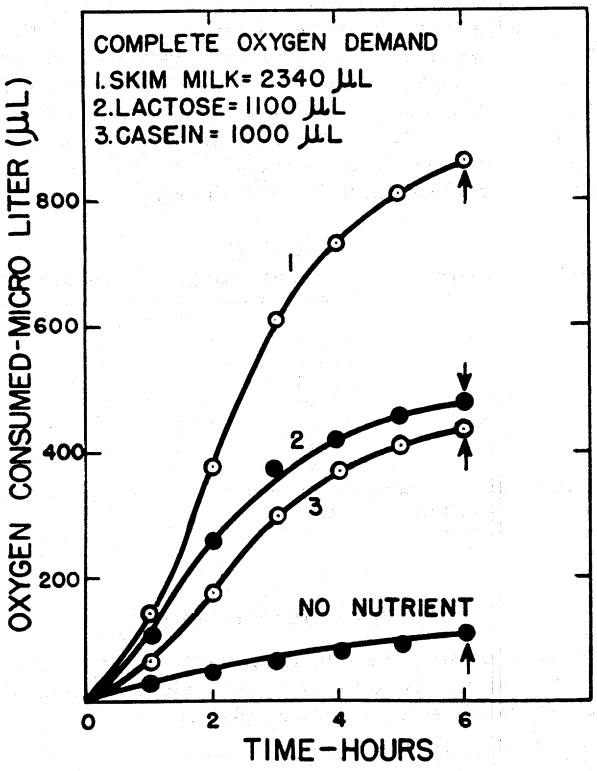

FIGURE 2. OXYGEN CONSUMED WHEN SKIM MILK, LACTOSE, AND CASEIN ARE ADDED IN RESPIROMETER.
(Reprinted from Sewage and Industrial Wastes)

All organic nutrients were removed from the solution, but calculations based upon the theoretical oxygen demand and upon the actual amount of oxygen utilized failed to show complete oxidation of the substrate. Table III summarizes data showing that only 43% of the C.O.D. of lactose and casein and 37% of the skim milk were oxidized. The theoretical values were calculated from the composition of lactose and casein. The skim milk contained 36.3% casein and 50% lactose[5].

TABLE III
Oxygen Utilized in Bio-Oxidation

	Weight of sample micro-gm	Total Oxygen Value Microliter	Oxygen Used Microliter	Oxygen Used %
Skim milk	3000	2340	866	37
Lactose	1500	1113	479	43
Casein	1050	1000	430	43

Apparently 57 to 63% of the C.O.D. of the original organic matter was assimilated, while the remainder was oxidized for energy. Thus the conversion was:

$$\text{Organic wastes} + O_2 \xrightarrow{\text{microbes}} \text{cells} + CO_2 + H_2O$$

Empirical Composition of Sludge Cells

The oxidation of organic material requires many intricate steps before the ultimate cell is produced. However, in order to follow the biological oxidation and determine oxygen demand, cell synthesis was expressed in a simple way[10]. Analyses were made for the elements shown in Table IV. Each element was calculated to its molar basis by dividing the percent of component found by its atomic weight. The resulting formula $C_5H_7NO_2$ was a gross over-simplification of the organized system of the microbial cells. The mole weight of this cell was 113 without ash and 124 atom units with the ash.

TABLE IV
Empirical Composition of Aerated Sludge Organisms

Component	Proportion	Ratio of atoms % /atomic wt.	
C	47.26	3.94	4.9*
H	5.69	5.65	7.0
N	11.27	0.81	1
O	27.0	1.69	2.1
Ash	8.61		

*N considered as a single atom.
Empirical formula = $C_5H_7NO_2$

Sugar Conversion to Cells

The early studies showed that sugar was either completely oxidized or converted to cell tissue, since products of incomplete oxidation were absent. The energy-yielding step oxidized the sugar completely, thus:

$$C_{12}H_{22}O_{11} \cdot H_2O + 12\ O_2 \longrightarrow 12\ CO_2 + 12\ H_2O$$

or expressed more conveniently:

$$CH_2O + O_2 \longrightarrow CO_2 + H_2O$$
$$\text{R.Q.} = 1/1 = 1.0$$

The R. Q., or respiration quotient, showing the ratio between oxygen utilized and carbon dioxide evolved agreed well with the experimental value of 1.04. The remaining equations gave similar agreement.

Production of cell tissues using ammonia as a nitrogen source was equated:

$$5\ (CH_2O) + NH_3 \longrightarrow C_5H_7NO_2 + 3\ H_2O$$

Since 37% of the theoretical amount of oxygen was used during assimilation, only 3/8 or 37.5% of the sugar was completely oxidized while 5/8 or 62.5% was assimilated:

$$8\ CH_2O + 3\ O_2 + NH_3 \longrightarrow C_5H_7NO_2 + 3\ CO_2 + 6\ H_2O$$
$$\text{R.Q.} = 3/3 = 1.0$$

The yields by weight were also consistent with laboratory results. 8 (CH_2O) or 240 atom units yielded $C_5H_7NO_2$ or 113 atom units or 124 atom units when ash was included. This gave 52% yield by weight and approximated those obtained in earlier experiments.

Protein Conversion to Cells

The protein casein, had the formula $C_8H_{12}N_2O_3$ omitting P and S and had a "mole" weight of 184. Casein may be completely oxidized thus:

$$C_8H_{12}N_2O_3 + 8\ O_2 \longrightarrow 8\ CO_2 + 2\ NH_3 + 3\ H_2O$$
$$R.Q. = 8/8 = 1.0$$

Assimilation to cell tissue according to manometric data showed that 3 carbons were completely oxidized while 5 carbons were assimilated:

$$C_8H_{12}N_2O_3 + 3\ O_2 \longrightarrow C_5H_7NO_2 + NH_3 + 3\ CO_2 + H_2O$$
$$R.Q. = 3/3 = 1.0$$

Skim Milk Conversion to Cells

The above equations showed that a mole of cell substance was produced from 240 units of sugar or from 184 units of casein. Since this was the same proportion as found in skim milk, the two equations were added to give:

$$8\ (CH_2O) + C_8H_{12}N_2O_3 + 6\ O_2 \longrightarrow 2\ C_5H_7NO_2 + 6\ CO_2 + 7\ H_2O$$
$$R.Q. = 6/6 = 1.0$$

The last equation showed that the yield of cells would be 2 x 124/240 + 184 or 58.5% of the skim milk solids. This was somewhat higher than the 52% observed in experiments. The difference may be the result of endogenous respiration.

Endogenous Respiration

Unfed or starving cells had a low oxygen demand. The organisms oxidized their own tissue:

$$C_5H_7NO_2 + 5\ O_2 \longrightarrow 5\ CO_2 + NH_3 + 2\ H_2O$$
$$R.Q. = 5/5 = 1.0$$

If oxidation continues long enough, the accumulated sludge digests itself[6]. The equation shows that 1 mole of cell with a formula weight of 113 requires 160 weight units of oxygen. Endogenous respiration proceeded at a QO_2 of 10. In other words 10 microliters of oxygen were used per mg cells per hour. This calculated to 14.3 micrograms oxygen and from the above relationship represented the destruction of 10.2 micrograms of cell tissue. This amount of tissue was equal to 1% of the original mg of cells. Rates as high as 1.25% per hour were observed in field trials[12].

Oxygen Utilization

Polarographic studies showed that the rate of oxidation was fairly constant above a concentration of 100 ppm waste when 500 ppm sludge was used[10]. The time necessary for oxidation of the waste would be directly proportional to the concentration above 100 ppm. This study also showed that an oxygen concentration of 0.35% to 0.5 ppm was necessary to prevent anaerobic conditions.

The rate and extent of oxidation were also determined on vigorously aerated mixtures by passing the spent air through barium hydroxide and measuring the CO_2 evolved[15]. Figure 3 shows the results of such an experiment. The rate of oxidation during assimilation was about 10 times that of the endogenous respiration of the unfed sample[6]. Again, in 6 to 7 hours the rate had dropped and oxygen demand was low.

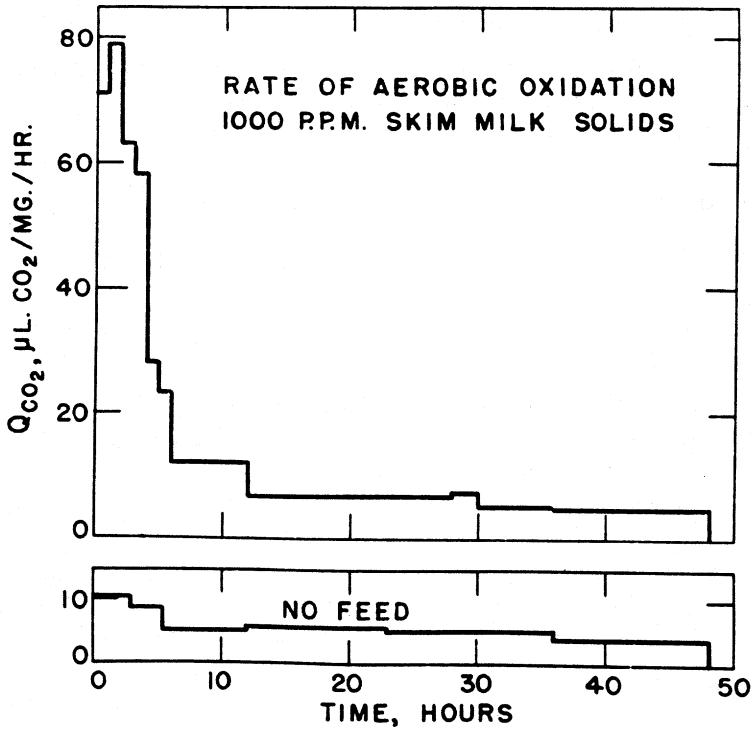

FIGURE 3. CO_2 PRODUCTION PER MG. SLUDGE WHEN 1000 PPM MILK SOLIDS WERE ADDED TO 410 PPM SLUDGE. LOWER SECTION SHOWS ENDOGENOUS RESPIRATION OF UNFED SLUDGE
(Reprinted from Sewage and Industrial Wastes)

Application of Data

The information thus obtained in the laboratory makes it possible to calculate the amount of sludge produced in the aeration process and the quantity of oxygen needed to produce the sludge. Further, it is possible to determine the rate at which oxygen must be supplied. The amount of sludge that is oxidized also may be determined.

The following calculations made on 1 pound of skim milk dissolved in 1000 pounds of water in the presence of 500 ppm sludge may be applicable to other wastes. The total theoretical amount of oxygen needed for complete oxidation of the skim milk is 1.214 pounds.

In the assimilation phase:

Part of total O_2 required	37.5%
Quantity O_2 needed	0.453 lb.
Time required	6.0 hours
Hourly oxygen requirement	0.075 lb.
Cells produced	0.5 lb.

In the endogenous phase:

Part of total O_2 required	62.5%
Quantity O_2 needed	0.761 lb.
Time required to oxidize cells	100 hours
Hourly oxygen requirement	0.007 lb.

The tabulation shows that conditions can be established to avoid accumulation of sludge. If 2500 ppm sludge solids were carried in the aerator, 500 ppm would disappear by endogenous respiration in 20 hours; that is 1% per hour. The addition of 1000 ppm skim milk at that time would replace the cells that were destroyed, since this amount of milk produces 500 ppm cells. Such a process using a fill-and-draw method could be repeated indefinitely.

Dairy Waste Disposal

A simplified, almost fully automatic waste disposal system to handle 25,000 gallons dairy waste daily has been in operation for about a year. Its construction and operation have been described[13]. The waste is added as it comes from the plant and the tank is continuously aerated for a number of hours. Aeration is then stopped and the sludge is allowed to settle for 1 to 2 hours. The supernatant, clear liquid flows from the tank from an outlet above the sludge surface. The valve is closed and slight aeration is introduced until waste from the dairy enters the tank in the morning when the cycle begins again. A larger installation has also been working successfully[14]. Investigations are continuing at The Pennsylvania State University on the fill-and-draw, as well as the continuous, process.

Air Supply

The rapid bio-oxidation process as shown by the graphs and data has a very high oxygen demand. This must be satisfied during removal and assimilation of the waste in order to keep the process aerobic and running smoothly. Satisfactory means of supplying this air in industrial installations has been an engineering difficulty. Sufficient aeration was accomplished by means of ejectors, which act similarly to water aspirators and intimately mix the air with waste[14]. Another operation has been devised for fruit wastes using equipment that attains thorough mixing by aeration and mechanical agitation[2].

The relatively high concentrations of organic matter in industrial wastes and the high oxygen demand during removal and assimilation by microorganisms make it mandatory that more efficient means of air supply and dispersion are necessary than are usually required for municipal wastes. High oxygen transfer from the air to the solution is possible with equipment now available.

Summary

The results of these investigations are summarized in Figure 4. A strong organic waste requires considerable oxygen during the assimilation phase. The time of assimilation varies directly with the strength of the waste and inversely with sludge concentration. The plotted values in Figure 4 were obtained using 1000 ppm milk solids and 500 ppm sludge cells. As much as 80 ppm oxygen are required per hour. If 1000 ppm sludge were used, the rapid oxygen demand would subside in 3 hours instead of 6 hours. During this period the soluble wastes disappear and about one-half of the waste is converted to cell material as shown by the curve.

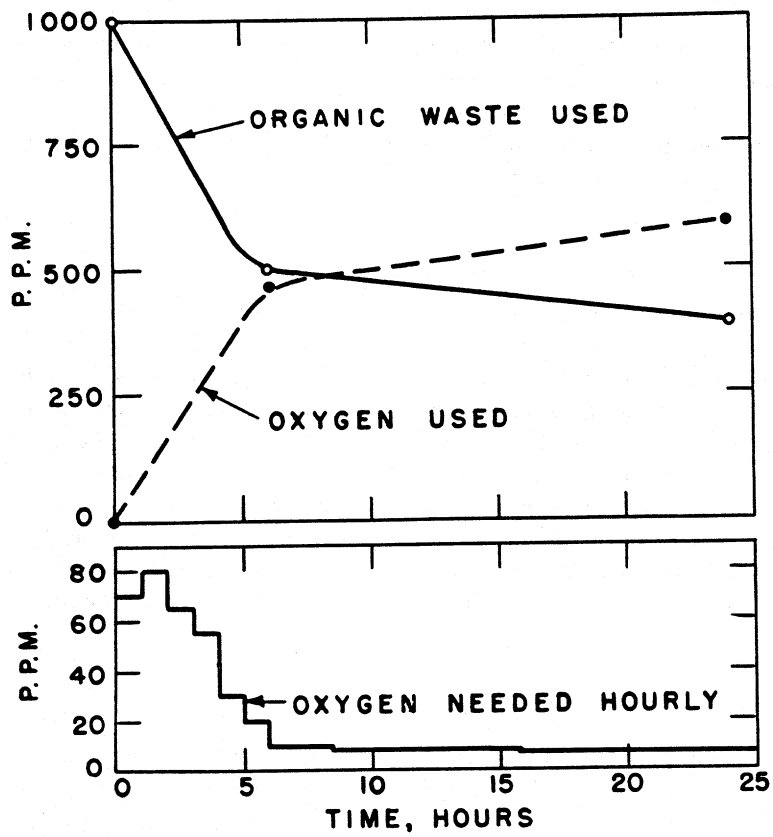

FIGURE 4. GRAPH SUMMARIZING DATA, SHOWING REDUCTION OF 1000 PPM C.O.D. OF MILK BY 500 PPM SLUDGE AND HOURLY OXYGEN REQUIREMENTS.

After removal and conversion to cells, a second phase sets in that requires only about one-tenth as much oxygen per hour. This is the endogenous phase wherein the sludge oxidizes itself at the rate of 1% per hour with a low oxygen demand.

Equations explaining these changes are given. Some applications of the data and a short description of an industrial installation have been presented.

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